

# Unprecedented Formation of $\mu$ -Vinylidene Complexes from Phospha-ruthenocene and Acyl Chloride via Activation of the C=O Double Bond

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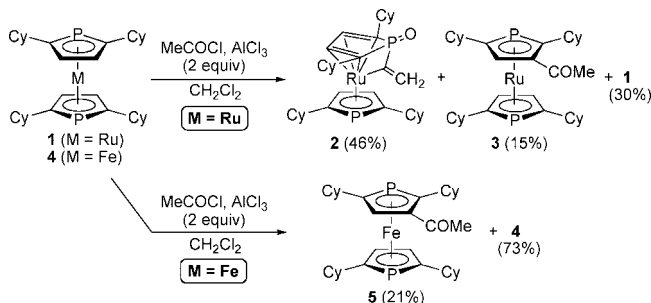
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**Summary:** A novel reaction mode of phosphametallo-cenes was discovered. The phospha-ruthenocenes with cyclohexyl substituents at the  $\alpha$ -positions of the  $\eta^5$ -phospholide(s) reacted with acyl electrophiles by an initial electrophilic attack to the ruthenium to produce the  $\mu$ -alkenylidene species with activation of the acyl C=O double bond and elimination of an  $\alpha$ -hydrogen.

Recently, phosphametallo-cenes have attracted considerable attention in organometallic chemistry.<sup>1</sup> Because a phosphorus atom in an  $\eta^5$ -phospholide possesses a lone pair on it, phosphametallo-cenes are Lewis basic. Thus, they have been utilized as nucleophilic catalysts<sup>2</sup> or a new class of P-donor ligands with unique electronic/steric properties.<sup>3,4</sup> Although many interesting applications of these compounds have been reported so far, studies on their reactivity are still relatively limited. In general, phosphametallo-cenes are "aromatic", as seen in ( $\eta^7$ -cyclo-pentadienyl)metal complexes, and serve as good substrates for electrophilic substitution reactions,<sup>5</sup> such as Friedel–Crafts

## Scheme 1. Reactions of Diphosphametallo-cenes with Acetyl Electrophile



acylation or Vilsmeier formylation. In this report, we would like to describe an unprecedented reaction of phosphametallo-cene species. During our studies on reactivity of phospha-ruthenocenes,<sup>41,67</sup> it was found that a reaction between a phospha-ruthenocene and an acyl electrophile produced a novel  $\mu$ -vinylidene species, where the vinylidene moiety bridged the Ru center and the phosphorus atom, via activation of the acyl C=O double bond.

Treatment of the 1,1'-diphospha-ruthenocene **1** with 2 equiv of an acetyl electrophile, which was generated from  $\text{CH}_3\text{COCl}$  and  $\text{AlCl}_3$ , in refluxing dichloromethane for 24 h gave the pale yellow crystalline product **2** in 46% yield together with recovered **1** (30%) and a small amount of the Friedel–Crafts acetylation product **3** in 15% yield (Scheme 1, top). The products **2** and **3** were air- and moisture-stable and easily purified by silica gel column chromatography. The product **2** showed two signals of equal intensity at  $\delta$  -26.6 and -21.2 in the  $^{31}\text{P}$  NMR spectrum. The  $^1\text{H}$  NMR spectrum of **2** showed four doublets in the olefinic/phospholyl region [ $\delta$  5.40 (d,  $J_{\text{PH}} = 3.9$  Hz, 2H), 5.55 (d,  $J_{\text{PH}} = 17.0$  Hz, 2H), 6.02 (d,  $J_{\text{PH}} = 64.1$  Hz, 1H), 6.83 (d,  $J_{\text{PH}} = 35.5$  Hz, 1H)] with a 2:2:1:1 integration ratio. In the phosphorus-decoupled  $^1\text{H}$  NMR spectrum, these four signals are turned into four singlets. The HRMS

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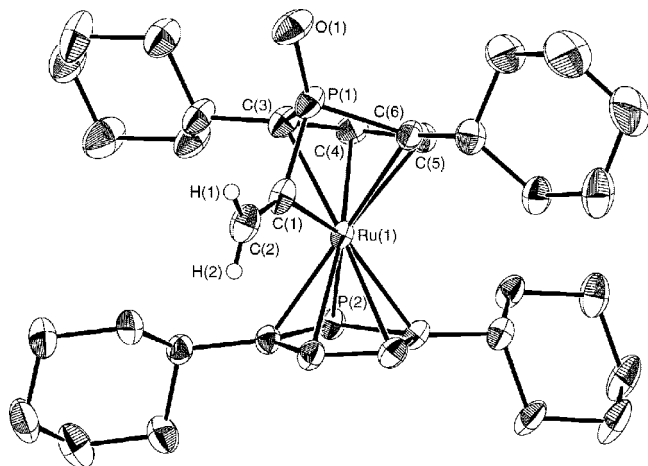
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**Figure 1.** ORTEP drawing of **2** with 30% thermal ellipsoids. All hydrogen atoms except H(1) and H(2) are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ru(1)–P(1) (nonbonding) = 2.6360(11), Ru(1)–P(2) = 2.4345(10), Ru(1)–C(1) = 2.152(4), P(1)–C(1) = 1.747(4), P(1)–O(1) = 1.479(3), C(1)–C(2) = 1.315(6); Ru(1)–C(1)–P(1) = 84.42(17), C(3)–P(1)–C(6) = 93.03(19), Ru(1)–C(1)–C(2) = 141.8(3), P(1)–C(1)–C(2) = 133.7(3).

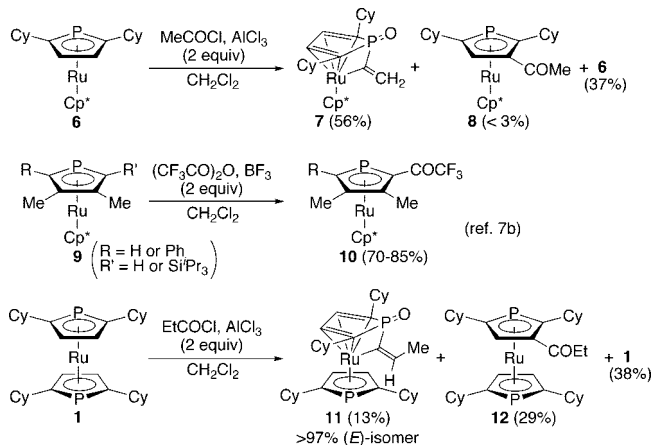
analysis suggested a chemical formula of  $C_{34}H_{50}OP_2Ru$  for **2**, which was identical to that of the Friedel–Crafts acetylation product **3**.

Recrystallization of **2** from hot ethyl acetate grew prismatic crystals suitable for X-ray structure analysis. The result of the crystallography is shown in Figure 1. One of the two phospholyl ligands in **2** is oxidized at P(1), and the phosphorus shows distorted tetrahedral geometry. There is no bonding interaction between Ru(1) and P(1) with the Ru(1)–P(1) distance of 2.6360(11) Å. The P(1)C(3)C(4)C(5)C(6) core coordinates to Ru(1) at the  $\eta^4$ -diene moiety with the envelope-like bent structure; the dihedral angle between the P(1)C(3)C(6) plane and the C(3)C(4)C(5)C(6) plane is 16.33°, and P(1) lies out of the C(3)C(4)C(5)C(6) plane by 0.360 Å away from Ru(1). The vinylidene moiety C(1)=C(2)H(1)H(2) bridges between Ru(1) and P(1). The C=CH<sub>2</sub> plane is nearly perpendicular to the  $\eta^5$ -phospholyl plane (85.50°), which makes the two hydrogens at the vinylidene terminus inequivalent to each other. The C(1)–C(2) bond length is 1.315(6) Å, that is, within a normal range for typical C=C double bonds. Analogous  $\eta^4$ -coordination of a *P*-oxo-phospholide can be seen in an iron complex reported by Mathey and co-workers.<sup>8</sup>

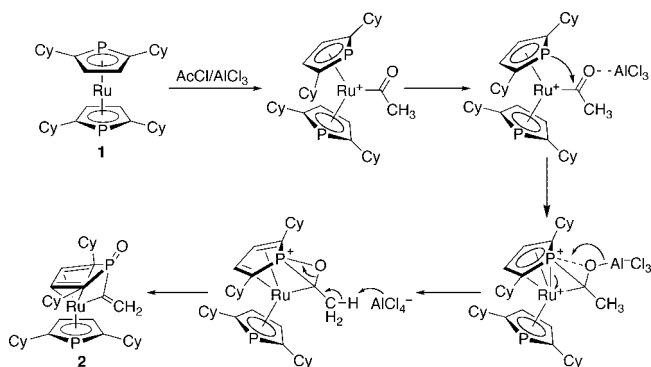
With free rotation of the  $\eta^5$ -phospholyl ligand around the Ru(1)–phospholyl axis, complex **2** is  $C_s$  symmetric in solution, and the <sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P NMR spectra are consistent with the solid-state structure.

The origin of O(1) and the  $\mu$ -vinylidene could be ascribed to acetyl chloride; that is, the phosphorus and the ruthenium atoms in **1** cooperatively activated the C=O double bond in CH<sub>3</sub>COCl during the transformation to **2**. The ruthenium center and the cyclohexyl substituents at the  $\alpha$ -positions of the phospholides in **1** play important roles for formation of this unique  $\mu$ -vinylidene complex **1**. Treatment of the homologous diphosphaferrrocene **4**, which is isostructural to **1**, under the identical conditions afforded the Friedel–Crafts acetylation product **5** in 21% yield (Scheme 1, bottom). Complex **5** was the sole detectable product, and the unreacted **4** was recovered in 73% yield. It was reported that the  $\alpha$ -positions of  $\eta^5$ -phospholides

## Scheme 2. Scope and Limitation of Preparing $\mu$ -Alkenylidene Ruthenium Complexes



## Scheme 3. Possible Reaction Pathway of Formation of **2** from **1** and AcCl/AlCl<sub>3</sub>



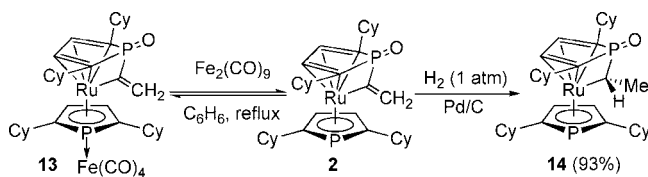
in phosphaferrrocenes were more reactive than the  $\beta$ -positions to electrophilic substitution.<sup>9</sup> The low yield of **5** can be attributed to the cyclohexyl groups, which block the more reactive  $\alpha$ -sites in **4**. The unfavorable formation of **3** in the reaction of **1** (Scheme 1, top) could be partly ascribed to the shielding of the  $\alpha$ -phospholyl positions in **1** by the four Cy groups in the same way. Indeed, monophosphaferrrocenes **9**, which had an  $\alpha$ -hydro- or an  $\alpha$ -silyl-phospholide, were reported to be active substrates for the Friedel–Crafts acylation with  $(CF_3CO)_2O/BF_3 \cdot OEt_2$ , and the corresponding  $\alpha$ -trifluoroacetylphosphaferrrocene species **10** were obtained in good yields (Scheme 2, middle).<sup>7b</sup> On the other hand, the monophosphaferrrocene species **6** provided the  $\mu$ -vinylidene species **7** in 56% yield by the reaction with  $CH_3COCl/AlCl_3$ . The structure of **7** was unambiguously determined by various NMR measurements and X-ray crystallography (see Supporting Information). The formation of the  $\mu$ -vinylidene complex **7** is more selective for **6**: a Friedel–Crafts acetylation product **8** was obtained in less than 3%, and the unreacted **6** was recovered in 37% yield (Scheme 2, top).

The use of propionyl chloride for a reaction with **1** under otherwise identical conditions also afforded the  $\mu$ -alkenylidene species **11** albeit in low yield (13%). Complex **11** was obtained as the *E*-isomer predominantly (*E/Z* = >97/<3 determined by <sup>1</sup>H and <sup>31</sup>P NMR; Scheme 2, bottom).

A possible mechanism for the formation of the  $\mu$ -vinylidene complex **2** is shown in Scheme 3. Because all the  $\alpha$ -phospholide positions are blocked by the cyclohexyl substituents in **1**, the acetyl electrophile attacks the ruthenium center instead of the

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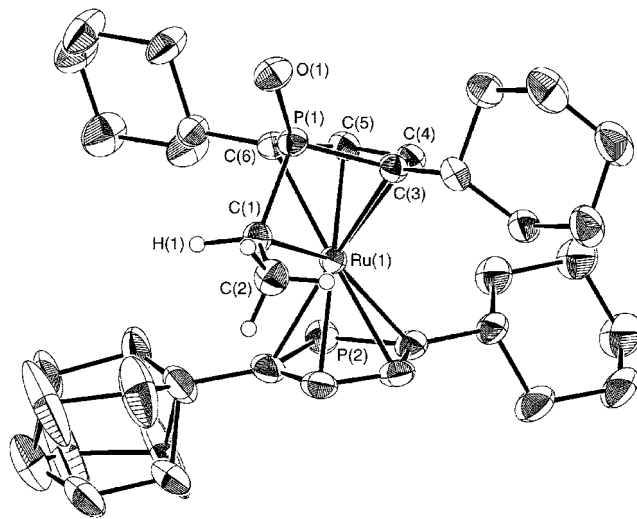
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Scheme 4. Reactivity of  $\mu$ -Vinylidene Complex **2**

$\eta^5$ -phospholide.<sup>10</sup> An intramolecular nucleophilic attack of the phospholide at the acetyl carbonyl carbon, which may be activated by  $\text{AlCl}_3$ , followed by a nucleophilic abstraction of one of the hydrogens in the acetyl moiety by the  $\text{AlCl}_4^-$  anion affords the  $\mu$ -vinylidene complex **2**. The final step in Scheme 3 is somewhat similar to the mechanism of the well-known Arbuzov reaction. Apparently, the orientation of the electrophilic (ruthenium) and the nucleophilic (phosphorus) sites in close proximity is an important factor in realizing the reaction.

Complex **2** possesses a lone pair on the phosphorus of the  $\eta^5$ -phospholide. Indeed, treatment of **2** with excess  $\text{Fe}_2(\text{CO})_9$  in boiling benzene- $d_6$  showed a partial conversion (ca. 50%) into the  $\text{Fe}(\text{CO})_4$  adduct **13**.<sup>11</sup> The  $^1\text{H}$  NMR spectrum of the mixture of **2** and **13** showed broadened resonances due to a slow exchange between the two (Scheme 4). Although **13** was not isolable because of weak coordination of **2** to the iron atom, the downfield shift of one of the two signals in the  $^{31}\text{P}$  NMR spectrum clearly indicated the coordination of the  $\text{Fe}(\text{CO})_4$  fragment in **13**.<sup>12</sup>

The  $\text{C}(1)\text{--}\text{C}(2)$  bond length and the  $\text{H}(1)\text{C}(2)\text{H}(2)$  angle ( $114(4)^\circ$ ) suggest olefinic character of the  $\mu$ -vinylidene moiety in **2**. Indeed, the  $\text{C}=\text{C}$  double bond is smoothly hydrogenated under 1 atm of  $\text{H}_2$  in the presence of Pd/C to give the  $\mu$ -ethylidene complex **14** in 93% isolated yield (Scheme 4). The X-ray crystal structure of **14** is shown in Figure 2. The  $\text{C}(1)$  atom, which bridges between  $\text{P}(1)$  and  $\text{Ru}(1)$ , changes its hybridization mode from  $\text{sp}^2$  to  $\text{sp}^3$  upon hydrogenation of the  $\text{C}(1)=\text{C}(2)$  double bond in **2**. Thus, some distortion can be detected in the local structure around  $\text{C}(1)$  in **14**. The overall structure of **14** is, however, very similar to that of **2**. Complex



**Figure 2.** ORTEP drawing of **14** with 30% thermal ellipsoids. All hydrogen atoms except for those on  $\text{C}(1)$  and  $\text{C}(2)$  are omitted for clarity. Selected bond lengths ( $\text{\AA}$ ) and angles (deg):  $\text{Ru}(1)\text{--}\text{P}(1)$  (nonbonding) = 2.6103(10),  $\text{Ru}(1)\text{--}\text{P}(2)$  = 2.4278(14),  $\text{Ru}(1)\text{--}\text{C}(1)$  = 2.229(4),  $\text{P}(1)\text{--}\text{C}(1)$  = 1.760(4),  $\text{P}(1)\text{--}\text{O}(1)$  = 1.484(3),  $\text{C}(1)\text{--}\text{C}(2)$  = 1.510(7);  $\text{Ru}(1)\text{--}\text{C}(1)\text{--}\text{P}(1)$  = 80.83(17),  $\text{C}(3)\text{--}\text{P}(1)\text{--}\text{C}(6)$  = 97.03(19),  $\text{Ru}(1)\text{--}\text{C}(1)\text{--}\text{C}(2)$  = 121.9(3),  $\text{P}(1)\text{--}\text{C}(1)\text{--}\text{C}(2)$  = 119.7(3).

**14** is insensitive to both oxygen and moisture and can be handled in air without appreciable decomposition.

In summary, an unprecedented reaction mode of phosphametalloenes was discovered. The phospharuthenocenes, which have 2,5-dicyclohexylphospholide(s), react with an acetyl or a propionyl electrophile by an initial electrophilic attack at the ruthenium and afford the  $\mu$ -alkenylidene species with activation of the acyl  $\text{C}=\text{O}$  double bond and elimination of an  $\alpha$ -hydrogen.

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**Supporting Information Available:** Detailed experimental procedures, compound characterization data, and crystallographic data in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(12) **2**,  $^{31}\text{P}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$ –26.4 and –19.3; **13**,  $^{31}\text{P}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$ –16.2 and 38.2.